

THE CHEMICAL GENERATION OF CARBENE ANION RADICALS

by

KUO-WEI LIN

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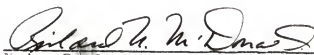
Department of Chemistry

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1978

Approved by:


Major Professor

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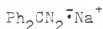
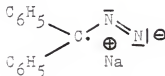
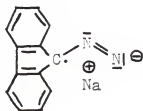
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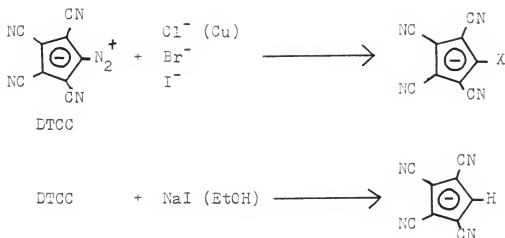
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INTRODUCTION

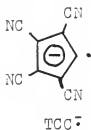
The reactions of diphenyldiazomethane (Ph_2CN_2) and 9-diazo fluorene (FlN_2) with powdered sodium in ether under N_2 atmosphere were reported by Kauffman and Hage.¹ Hydrolysis of the deep-blue solution derived from FlN_2 gave 9,9'-bifluorenyl (FlH-FlH) (32%) and in the presence of oxygen 9,9'-bifluorenylidene (Fl=Fl) (28%) and fluorenone azine ($\text{Fl=N}\cdot$) (34%) were produced. The deep-blue reduction solution obtained from Ph_2CN_2 and sodium in ether behaved similarly upon hydrolysis. The proposed reaction intermediates were diazo anion radical-sodium complexes, $\text{FlN}_2\cdot\text{Na}^+$ and $\text{Ph}_2\text{CN}_2\cdot\text{Na}^+$, respectively.



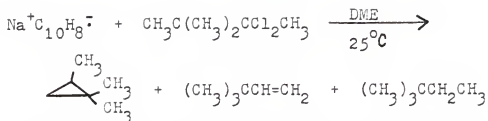
Webster² reported that sodium iodide or bromide reacted with diazotetracyanocyclopentadiene (DTCC) to give halotetracyanocyclopentadiene, while sodium chloride required copper as a catalyst. If methanol or ethanol was present, the only product isolated, even with sodium iodide, was tetracyanocyclopentadienide. The mechanisms of these substitution-reductions appeared to be free radical.



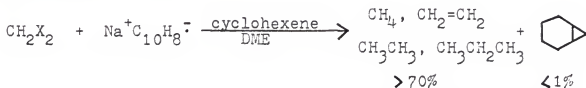
In the above reactions the tetracyanocyclopentadienylide anion radical ($\text{TCC}^{\cdot-}$) was proposed as the intermediate and could be generated polarographically at 0.23 V vs. SCE in acetonitrile or by mild reducing agents, such as copper powder, cuprous ion, or zinc powder. The structure of $\text{TCC}^{\cdot-}$ was considered to be a π -anion δ -radical ($\pi^2\delta^1$).



The reduction of 1 M 2,2-dichloro-3,3-dimethylbutane with 1 M sodium naphthalene ($\text{Na}^+\text{C}_{10}\text{H}_8^-$) in 1,2-dimethoxyethane (DME) at 25°C was reported by Sargent, et al.,³ to yield 1,1,2-trimethylcyclopropane (19%), 3,3-dimethyl-1-butene (38%) and 3,3-dimethylbutane (11.5%). It was proposed that tert-butylmethylcarbene was generated and was further reduced to the carbene anion radical at a rate competitive with that of intramolecular C-H insertion.



Additional evidence for the formation of carbene anion radicals came in the reductions of methylene dihalides. Sargent, et al.,⁴ reported that the reduction of CH_2Cl_2 in 60:40 (v/v) cyclohexene-DME with excess sodium naphthalene ($\text{Na}^+\text{C}_{10}\text{H}_8^-$) yielded low molecular weight hydrocarbons, such as, CH_4 , $\text{CH}_2=\text{CH}_2$, CH_3CH_3 , and $\text{CH}_3\text{CH}_2\text{CH}_3$, as the principal products of the reaction (>70%) and norcaradiene in yields of less than 1%. Alkylated naphthalenes and dihydronaphthalenes were also found in less than 30% yield.



The low yield of norcaradiene from the above reaction led to the conclusion that the rate of formation of methylene anion radical (CH_2^-) must be greater than that of the formation of norcaradiene and that CH_2^- must not itself readily add to cyclohexene. This was in keeping with Sargent's previous suggestion that tert-butylmethylcarbene could be reduced to the corresponding carbene anion radical at a rate competitive with that of intramolecular C-H insertion by the carbene.³ The constant, relative yield of ethylene generated by the reaction of the three methylene halides (CH_2X_2 , X = Cl, Br, or I) with sodium naphthalene indicated that CH_2^- could dimerize to form ethylene

dianion, followed by electron transfer with naphthalene, or that an $\text{CH}_2^{\cdot-}\text{-CH}_2\text{X}_2$ encounter could lead to formation of ethylene.

Lineberger, et al.,⁵ reported that $\text{CH}_2^{\cdot-}$ was generated by electron attachment to CH_2N_2 in the gas phase. The experiment of interest consisted of crossing a mass-analyzed $\text{CH}_2^{\cdot-}$ beam with an argon ion laser operating at 488 nm (2.540 eV) and measuring the kinetic energy of the electron photoejected. Coupled with ab initio calculations and a Franck-Condon factor analysis, the electronic structure of $\text{CH}_2^{\cdot-}$ was in good agreement with the experimental results. The structure of $\text{CH}_2^{\cdot-}$ ($^2\text{B}_1$) was determined to be $r_e \approx 1.1$ Å and $\theta_e \approx 100^\circ$, and the energy separation between $:\text{CH}_2$ ($^1\text{A}_1$) and $\dot{\text{C}}\text{H}_2$ ($^3\text{B}_1$) was found to be 19.5 ± 0.7 kcal/mol.

Recently, the electrochemical reduction of Ph_2CN_2 in 0.1 M DMF- $\text{Et}_4\text{N}^+\text{ClO}_4^-$ has been reported by McDonald, January, Borhani, and Hawley.⁶ The products were diphenylmethane (Ph_2CH_2), benzophenone azine ($\text{Ph}_2\text{C=N-N}_2$) and benzophenone ($\text{Ph}_2\text{C=O}$); the ketone was mistakenly identified as diphenylmethanamine (Ph_2CHNH_2) in the paper.⁶ Diphenylcarbene anion radical ($\text{Ph}_2\text{C}^{\cdot-}$) was generated at -1.68 V vs. SCE from the chemically irreversible reduction of Ph_2CN_2 . The results were believed to be consistent with a radical chain process. $\text{Ph}_2\text{C}^{\cdot-}$ was considered to behave primarily as a radical species in its reaction producing Ph_2CH_2 . Dimerization of $\text{Ph}_2\text{C}^{\cdot-}$ was ruled out as an important reaction channel since only trace amounts of tetraphenylethene ($\text{Ph}_2\text{C-CPH}_2$) and tetraphenylethane ($\text{Ph}_2\text{CH-CHPh}_2$) were detected by

chromatographic methods.

These results were quite different from those reported by Elofson, et al.,⁷ for the electrochemical reduction of Ph_2CN_2 in sulfolane. In this case the products were Ph_2CH_2 (40%), Ph_2CHNH_2 (20%), and nitrogen. However, the decomposition of $\text{Ph}_2\text{CN}_2^\cdot$ was suggested to occur by protonation to give $\text{Ph}_2\text{CHN}_2^\cdot$, which then either loses nitrogen to give benzhydryl radical and ultimately Ph_2CH_2 , or couples with benzhydryl radical to give azodiphenylmethane. Reduction of this azo compound was postulated to give Ph_2CHNH_2 .

Electrochemical reduction of FlN_2 in $\text{DMF}-(n\text{-Bu})_4\text{N}^+\text{ClO}_4^-$ afforded the azine, ($\text{Fl}=\text{N}_2$), in high yield (91±7%).⁸ Fluorenone ($\text{Fl}=\text{O}$) was observed as a minor product when electrolysis was effected in the presence of adventitious amounts of oxygen. Neither fluorene nor any dimeric product was detected by gas chromatography in other than trace amount (<0.5%). It was proposed that fluorenylidene anion radical ($\text{Fl}^\cdot$) was generated by reduction of FlN_2 at -1.35 V vs. SCE from fast, unimolecular, irreversible decomposition of $\text{FlN}_2^\cdot$. The increased production of the corresponding azine and concomitant decrease in the amount of hydrocarbon product from $\text{Fl}^\cdot$ compared to $\text{Ph}_2\text{C}^\cdot$ under similar electrochemical conditions was believed due to the dual relative reactivities of the two carbene anion radicals. Significantly, a reversible redox couple attributed to $\text{Fl}^\cdot/\text{Fl}$ was observed in this study.

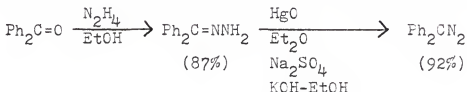
OBJECTIVES OF THIS INVESTIGATION

The objectives of this investigation were:

1. To explore certain chemical reductions of diazo compounds (R_2CN_2) to yield the corresponding carbene anion radicals.
2. To study solvent effects on radical vs anion reactivities of these carbene anion radicals.
3. To investigate the possibility that 9-fluorenyl anion would react with FlN_2 .

EXPERIMENTAL RESULTS

Using the procedure of Miller⁹, Ph_2CN_2 was synthesized as dark red crystals, mp $29-30^\circ\text{C}$, after recrystallization from petroleum ether (bp $35-60^\circ\text{C}$). Using double the volume of abso-



lute ethanol saturated with potassium hydroxide, the yield of Ph_2CN_2 could be increased to 92% compared to 89% in the old method. The ir and nmr spectra are consistent with the structure of Ph_2CN_2 . To prevent decomposition, Ph_2CN_2 was stored in a freezer. Since $(\text{Ph}_2\text{C}=\text{N})_2$ was a major product in the electrochemical reduction of Ph_2CN_2 ,⁶ the azine was prepared by reaction of Ph_2CN_2 with $\text{BF}_3\text{-Et}_2\text{O}$ in ether at 0°C ,¹⁰ and was obtained as pale yellow rods, mp $162-163^\circ\text{C}$, in 70% yield. The second expected product from reduction of Ph_2CN_2 , Ph_2CH_2 , was prepared by Wolff-Kishner reduction of benzophenone.¹¹ Other possible products, $\text{Ph}_2\text{CH-CHPh}_2$ (Columbia Organic), $\text{Ph}_2\text{C=CPh}_2$ (Aldrich), and Ph_2CHNH_2 (Aldrich), were purchased from commercial sources and their purities checked by mp, and ir and nmr spectroscopy.

The dark-green $\text{Na}^+\text{C}_{10}\text{H}_8^-$ solution was prepared from a mixture of sodium and excess naphthalene in THF at -12°C under an argon atmosphere according to the procedure of Vora and Holy.¹² The mixture was stirred under an argon atmosphere for over 24 hr before two 5-ml aliquots were removed, quenched in 50-ml portions of water, and titrated for total base with standardized hydrochloric acid solution to a phenolphthalein

end-point.

The first experiment was to add crystals of Ph_2CN_2 to the $\text{Na}^+\text{C}_{10}\text{H}_8^-$ solution in THF cooled to -12°C . After the solvent was removed, isolation of the products gave both $(\text{Ph}_2\text{C}=\text{N})_2$ and Ph_2CHNH_2 along with unknown residues.

The reduction of $(\text{Ph}_2\text{C}=\text{N})_2$ with excess $\text{Na}^+\text{C}_{10}\text{H}_8^-$ solution at -12°C under an argon atmosphere was carried out to yield Ph_2CHNH_2 in 98% yield after correcting for known loss of amine in the work-up procedure. The correction factor, 1.19 (100/-83.8), for recovered yield of amine was determined by following the same extraction procedure with a weighed amount of Ph_2CHNH_2 .

A solution of Ph_2CN_2 in dry THF in a pressure-equalized addition funnel was added dropwise to an excess of $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in THF, cooled to -12°C , over a period of 0.5 hr (runs 1-3, Table I). After distilled water was added, the color of the mixture changed from dark to light brown. The THF was evaporated and ether was added. The two-phase mixture was separated and the ether layer extracted with 10% HCl solution. The aqueous acidic solution was basified to pH ~13 with 10% NaOH solution and extracted with ether. The ether extracts were washed with distilled water, saturated NaCl solution, and dried. After solvent removal, Ph_2CHNH_2 was obtained and identified by use of ir and nmr spectroscopy, and mp of an amine derivative in comparison to those of authentic Ph_2CHNH_2 . Correcting the isolated yield of Ph_2CHNH_2 for known losses during work-up gave 83±2% yield of the amine.

Table I. Product Analysis for the Reaction of Ph_2CN_2 with Sodium Naphthalene Solution in THF at -12°C .

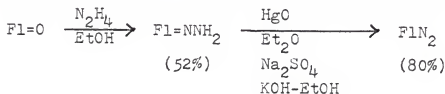
Run no.	Method of Addition	Ph_2CN_2 mM	$\text{Na}^+\text{C}_{10}\text{H}_8^-$ mM	Product, % Yield ^a	
				Ph_2CH_2 ^b	Ph_2CHNH_2 ^c
1	Slow ^d	15.7	62.8	13	84
2	Slow ^d	19.9	79.6	10	82
3	Slow ^e	15.8	159.0	17	85
4	Fast ^f	10.4	52.2	4	91
5	Fast ^f	10.3	51.6	5	93

^aTetraphenylethane and benzophenone azine were detected only in trace amounts by gas chromatography. ^bThese were obtained from calculation of ratio of aromatic hydrogens on nmr. ^cThese were corrected by multiplying the isolated yield by the recovery factor (1.19). ^dDropwise addition of Ph_2CN_2 in 150 ml of THF to $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in 400 ml of THF over a period of one hr. ^eDropwise addition of Ph_2CN_2 in 100 ml of THF to $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in 400 ml of THF over a period of 0.5 hr. ^fSyringe injection of Ph_2CN_2 in 10 ml of THF to $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in 200 ml of THF over a period of 5 sec.

The neutral products of the reaction were obtained. These products were separated by sublimation at 35°C and 0.2 torr. The nmr spectrum of the sublimate showed only the presence of naphthalene, 1,4-dihydronaphthalene, and Ph_2CH_2 . Since the nmr absorption of these three components are cleanly separated from one another, the amount of Ph_2CH_2 was determined to be $11 \pm 2\%$ for runs 1 and 2, Table I. In run 3, Table I, the $[\text{Na}^+\text{C}_{10}\text{H}_8^-]/[\text{Ph}_2\text{CN}_2]$ mole ratio was increased from 4 to 10 with an increase in the amount of Ph_2CH_2 (17%) produced. The residue remaining in the sublimation tube was checked by mass spectrometry and appeared to be polymeric dihydronaphthalene. Only trace amounts of $\text{Ph}_2\text{CH-CHPh}_2$ and $(\text{Ph}_2\text{C=N})_2$ were found in this residue by gas chromatography.

A solution of Ph_2CN_2 in dry THF was syringe injected into a solution of $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in THF, cooled to -12°C, over a period of 5 sec (runs 4 and 5, Table I). Isolation and identification of the products as described above in the slow additions resulted in Ph_2CHNH_2 ($92 \pm 1\%$) and Ph_2CH_2 ($5 \pm 1\%$).

The preparation of FlN_2 was similar to the method described above for the synthesis of Ph_2CN_2 .⁹ Recrystallization from petroleum ether (bp 35-60°C) gave orange-red needles, mp 94-95°C; the ir and nmr spectra agreed with this structure. To avoid decomposition, FlN_2 was stored in a freezer. Since



the electrochemical reduction of FlN_2 yielded $(\text{Fl}=\text{N})_2$ in high yield,⁸ it was prepared from a mixture of $\text{Fl}=\text{O}$, N_2H_4 (95%), and KOH-EtOH in ethanol.¹³ Recrystallization from xylene gave violet needles of $(\text{Fl}=\text{N})_2$, mp $268-269^\circ\text{C}$, in 80% yield. Another possible product from reduction of FlN_2 , 9,9'-bifluorenyl (FlH-FlH) was prepared in 15% yield by the reaction of $(\text{Fl}=\text{N})_2$ with N_2H_4 (95%) in the presence of KOH in diethylene glycol.¹³ FlH-FlH was obtained as white needles, mp $244-245^\circ\text{C}$, after recrystallization from benzene-ethanol (1:2). A third possible product, 9,9'-bifluorenylidene ($\text{Fl}=\text{Fl}$), was prepared in 91% yield from coupling of $\text{Fl}=\text{O}$ with McMurray's reagent ($4\text{TiCl}_3\text{-LiAlH}_4$).^{14,15} After recrystallization from $\text{CHCl}_3\text{-EtOH}$ (1:1), $\text{Fl}=\text{Fl}$ was obtained as orange needles, mp $194-195^\circ\text{C}$. The other expected product, fluorene (FlH_2) (Eastman), $\text{Fl}=\text{O}$ (Eastman), and 9-aminofluorene (FlHNNH_2) obtained from 9-aminofluorene hydrochloride (Aldrich), were purchased from commercial sources and their purities checked by mp, and ir and nmr spectroscopy. FlHNNH_2 was obtained from neutralization of 9-aminofluorene hydrochloride with 10% NaOH solution. Recrystallization of the amine from n-hexane yielded white needles, mp $64-65^\circ\text{C}$.

The reduction of $(\text{Fl}=\text{N})_2$ with excess $\text{Na}^+\text{C}_{10}\text{H}_8^-$ solution was carried out to yield FlHNNH_2 in 100% yield, after correcting for known losses of amine in the work-up procedure. The correction factor, 1.19 (100/83.8), was determined by following the same extraction procedure with a weighed amount of FlHNNH_2 .

The reductions of FlN_2 with excess $\text{Na}^+\text{C}_{10}\text{H}_8^-$ followed the

same procedures described above in the slow and fast additions of Ph_2CN_2 in dry THF to a THF solution of $\text{Na}^+\text{C}_{10}\text{H}_8^-$, and the results are listed in Table II. The same procedures for separation of the reaction products were applied to give FlHNNH_2 which was identified by comparison to the mp, and ir and nmr spectra of an authentic sample. Naphthalene and 1,4-dihydronaphthalene were removed by sublimation and the yellow residue contained FlH_2 (identified by nmr spectroscopy and glpc). The yield of FlH_2 was determined by adding 1,3,5-trinitrobenzene as an internal standard and integrating the nmr spectrum of this mixture. $\text{Fl}=\text{Fl}$ and $\text{FlH}-\text{FlH}$ were detected in trace amounts by glpc of this same residue. From the slow addition of FlN_2 , $40 \pm 2\%$ of FlH_2 and $53 \pm 3\%$ of FlHNNH_2 (runs 1 and 2, Table II) were obtained. Fast addition of FlN_2 led to a reduced amount of FlH_2 (12%) with a concomitant increase in the quantity of FlHNNH_2 (88%) (run 4, Table II). Run 3 is included in Table II to illustrate the dependence of the amount of the hydrocarbon FlH_2 produced on the amount of reducing agent present.

To investigate the effects of solvent on the nature of the reduction products, sodium in liquid ammonia (Na/NH_3) was examined as the reducing media with FlN_2 . The reaction between $(\text{Fl}=\text{N})_2$ and excess Na in liquid NH_3 failed to give FlHNNH_2 , but did lead to extensive ring reductions (Birch reduction). Thus, it was decided to run the reaction with a 1:1 FlN_2/Na mole ratio. The reaction of FlN_2 with Na/NH_3 solution under an argon atmosphere at -34°C was carried out to yield $\text{Fl}=\text{Fl}$ ($3 \pm 1\%$), $\text{FlH}-\text{FlH}$ ($4 \pm 1\%$), $(\text{Fl}=\text{N})_2$ ($79 \pm 0\%$), and $\text{Fl}=\text{O}$ ($6 \pm 1\%$) as listed in

Table II. Product Analysis for the Reaction of FlN_2 with Sodium Naphthalene Solution in THF at -12°C .

Run no.	Method of Addition	FlN_2 mM	$\text{Na}^+\text{C}_{10}\text{H}_8^-$ mM	Product, % Yield ^a		
				FlH_2 ^b	FlHNH_2 ^c	$(\text{Fl}=\text{N})_2$
1	Slow ^d	15.6	156.5	42	50	-
2	Slow ^d	15.1	151.0	39	55	-
3	Fast ^e	9.7	38.8	7	77	6
4	Fast ^e	11.3	112.3	12	88	-

^a9,9'-Bifluorenylidene and 9,9'-bifluorenyl were found in trace amounts by gas chromatography. ^bEmploying 1,3,5-trinitrobenzene as an internal standard in the nmr determination. ^cCorrected for recovery factor (1.19). ^dDropwise addition of FlN_2 in 100 ml of THF to $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in 400 ml of THF over a period of 0.5 hr. ^eSyringe injection of FlN_2 in 10 ml of THF to $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in 200 ml of THF over a period of 5 sec.

Table III. Product Analysis for the Reaction of FlN_2 with Na/NH_3 Solution at -34°C by Fast Syringe Injection Method.

Run no.	Na/NH_3 ^a mM	FlN_2 ^b mM	Product, % Yield ^c			
			Fl=O	Fl=Fl	FlH-FlH	$(\text{Fl=N})_2$
1	10.2	10.2	6	4	4	79
2	10.2	10.4	7	3	5	79

^aAssumed the reaction of Na with 100 ml of NH_3 was 100%. ^bIn 10 ml of THF. ^cSeparation of these components was achieved by silica gel column chromatography.

Table IV. Product Analysis for the Reaction of FlN_2 with 9-Fluorenyl Anion in 100 ml of THF at -12°C .

Run no.	FlN_2 mM	FlH_2 mM	PhLi mM	Product, mM ^a		
				FlH_2	FlH-FlH	$(\text{Fl=N})_2$
1	11.0	15.1 ^b (10.8)	10.8	11.7 ^b (7.4)	-	6.5
2	10.9	12.5 ^b (10.9)	10.9	7.2 ^b (5.6)	0.3	6.6

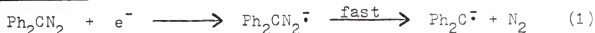
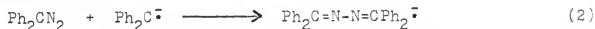
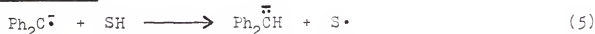
^aThe two major components were separated by column chromatography; a trace amount of Fl=Fl was found by glpc of the original mixture. ^bThese values represent those corrected for the excess FlH_2 originally employed.

Table III. The products were separated by silica gel column chromatography.

To determine if 9-fluorenyl anion (FlH^-) would react with FlN_2 , FlH^- was prepared ($\text{FlH}_2 + \text{PhLi}$ in THF) and allowed to react with FlN_2 in THF under an argon atmosphere at -12°C . The products were FlH_2 , $(\text{Fl}=\text{N})_2$, and $\text{FlH}-\text{FlH}$ as listed in Table IV. The products were separated by silica gel column chromatography.

DISCUSSION OF EXPERIMENTAL RESULTS

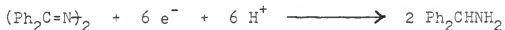
The results of the electrochemical reduction of Ph_2CN_2 were consistent with the radical chain process shown in Scheme I⁶. Propagation of the chain involved coupling of $\text{Ph}_2\text{C}^\cdot$ with

Scheme IInitiationPropagationTermination

Ph_2CN_2 to give $(\text{Ph}_2\text{C}=\text{N})_2^\cdot$ (reaction (2)), followed by electron transfer between Ph_2CN_2 and $(\text{Ph}_2\text{C}=\text{N})_2^\cdot$ to produce azine and $\text{Ph}_2\text{CN}_2^\cdot$ (reaction (3)). Loss of nitrogen from the latter species regenerated $\text{Ph}_2\text{C}^\cdot$, the chain carrying species. Termination of the chain occurred by reactions (5) and (6) in that sequence.

In addition, the present study involves the further reduction of $(\text{Ph}_2\text{C}=\text{N})_2$ to Ph_2CHNH_2 . This reduction is believed to be similar to that reported by Iund for the reduction of the closely related benzalazine.¹⁶ The reduction of $(\text{Ph}_2\text{C}=\text{N})_2$ by excess sodium or potassium produced an adduct containing 2-g atoms of alkali metal per mole of azine. After hydrolysis,

this gave N-benzhydryl benzophenone hydrazone in 54% yield.^{17a} However, lithium was shown to be capable of reducing $(\text{Ph}_2\text{C}=\text{N})_2$ to Ph_2CHNH_2 (76%) and $\text{Ph}_2\text{C}=\text{O}$ (20%) after work-up.^{17b} The ketone was believed to result from hydrolysis of $\text{Ph}_2\text{C}=\text{N}-\text{Li}$ and the amine from a "polylithio species", e.g. $\text{Ph}_2\text{CLi}-\text{NLi}_2$. This suggests that the overall stoichiometry in the azine to amine reduction is given by the equation,



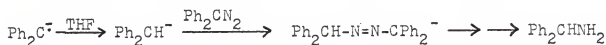
The reductions of Ph_2CN_2 by $\text{Na}^+\text{C}_{10}\text{H}_9^-$ in THF were carried out by adding a solution of diazo compound to the reducing agent. As shown in Table I, the variation of the mole ratio of reducing agent to Ph_2CN_2 from 4 to 10 in the slow, dropwise addition method did not have a major effect in the yields of the products, although a small increase in the yield of Ph_2CN_2 was observed. However, the different methods of addition did show a significant change in the product yields. As we can see, the yield of Ph_2CHNH_2 increases from 83±2% to 92±1% and that of Ph_2CH_2 decreases from 13±4% to 5±1% on changing from slow to fast addition. These results could be explained as due to the increased concentration of Ph_2CN_2 in which Ph_2C^- finds itself in the fast, syringe injection method. Thus, coupling to give azine anion radical becomes even more important. Since Ph_2CH^- may also react with Ph_2CN_2 to yield azine (as will be discussed with the reaction of FlH^- with FlN_2), the yield of Ph_2CH_2 may be a minimum value.

Although Ph_2CH^- has been produced in THF as a reactive intermediate to give excellent yields of products from its bi-

molecular reaction with other substrates,¹⁸ the lifetime of this basic species ($pK_a(\text{Ph}_2\text{CH}_2) = 33$)¹⁹ in THF under the present conditions has not been established. In the case of the slow addition method, the required lifetime may be several seconds to minutes as subsequent drops of Ph_2CN_2 in THF are added, and $\text{Na}^+\text{C}_{10}\text{H}_8^-$ and $\text{Ph}_2\text{CH}^-\text{Na}^+$ would then compete for the diazo compound.

The results appear to be consistent with those obtained by electrochemical reduction of Ph_2CN_2 .⁶ However, certain differences in the way the chemical and electrochemical experiments were carried out deserve comment at this point. The radical chain process depicted in Scheme I for the electrochemical reduction of Ph_2CN_2 may, in fact, not apply to the chemical reductions of this substrate especially in the slow, dropwise addition method. In this case, very small amounts of Ph_2CN_2 ($E_{p,c} = -1.68 \text{ V}$, $\text{DMF}-(n\text{-Bu})_4\text{N}^+\text{ClO}_4^-$ vs. SCE)⁶ are added to a large excess of the powerful reducing agent $\text{Na}^+\text{C}_{10}\text{H}_8^-$ ($E_{p,c} = -2.46 \text{ V}$, $\text{DMF}-\text{Et}_4\text{N}^+\text{Br}^-$ vs. SCE).²⁰ Further, $(\text{Ph}_2\text{C}=\text{N})_2^{\cdot-}$ and $(\text{Ph}_2\text{C}=\text{N})_2^{2-}$ which serve as electron transfer-reducing agents in the electrochemical reduction (Scheme I) of Ph_2CN_2 are removed at unknown rates of reduction processes to finally yield Ph_2CHNH_2 .¹⁷ It is not known if the intermediates in this azine $\longrightarrow$ amine reduction can serve in electron transfer steps to Ph_2CN_2 . Also, the solvent in these chemical reductions, THF, is known to be a better hydrogen atom donor than DMF used in the electrochemical reductions.²¹ For these reasons, the chain length of the free radical chain reaction in

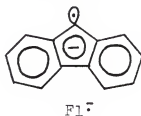
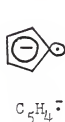
the chemical reductions must be considerably attenuated compared to that in the electrochemical reductions or the chain process may be nonexistent. This could mean that a principle source of azine (then to amine), especially in the slow drop-wise addition method, might be the following sequence.



This suggested pathway will be considered in the following discussion on the related reductions of FlN_2 .

The electronic structure of H_2C^- has been examined by ab initio^{5,22} and MINDO/3^{23a,24} calculations and is in excellent agreement with the estimated experimental structure derived from its photoelectron spectrum.⁵ The electronic configuration of H_2C^- is $\delta^2\pi^1$ (a δ -anion π -radical) with the H-C-H angle of about 100° which is structurally similar to the singlet of $:\text{CH}_2$. At this point, it is assumed that this is also approximately the structure of Ph_2C^- with both phenyl rings twisted about their C_1-C^- bonds to relieve nonbonded repulsions.

MINDO/3 calculations on cyclopentadienylidene anion radical (C_5H_4^-) show the ground state doublet to have a $\delta^1\pi^2$ electronic configuration.^{23a,25} It was assumed that this electronic configuration would also be that expected for the fluorenylidene anion radical (Fl^-), where fusion of the benzene rings onto C_5H_4^- would be expected to further separate the energies



of the δ - and π -orbitals of $C_5H_4^-$. Thus, the chemical reduction of FlN_2 was investigated to determine if the change in electronic configuration between Ph_2C^- and Fl^- would result in observable chemical differences.

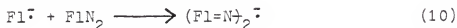
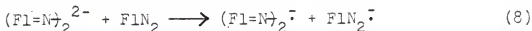
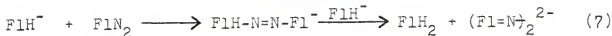
The reductions of FlN_2 by $Na^+C_{10}H_8^-$ in THF were carried out using the slow, dropwise and fast, syringe injection methods previously described for the reductions of Ph_2CN_2 . However, in the experiments to be considered here (runs 1, 2, and 4 in Table II), the $[Na^+C_{10}H_8^-]/[FlN_2]$ ratio of 10 was employed. With the slow addition method, FlH_2 (41 $\pm$ 2%) and $FlHNNH_2$ (53 $\pm$ 3%) were obtained. Use of the fast, syringe injection method led to a reduced amount of FlH_2 (12%) and an increase in the yield of $FlHNNH_2$ (88%). Run 3 illustrates the effect on the product distribution in the fast injection method when the ratio $[Na^+C_{10}H_8^-]/[FlN_2]$ was reduced to 4. The result was a decrease in the yield of FlH_2 (7%) and isolation of a small amount of azine (6%).

To demonstrate that the reaction



is not the only potential source of azine (and, therefore, of amine), 9-fluorenyl anion (FlH^-) was prepared in THF and allowed to react with one molar equivalent of FlN_2 (Table IV). The results are interpreted mechanistically in Scheme II. The initial concentration of FlH^- was consumed in its reaction with FlN_2 to form the conjugate acid of azine dianion followed by deprotonation (reaction (7)). The remaining FlN_2 (0.5 of original $[FlN_2]$) was then reduced by $(Fl=N)_2^{2-}$ (reaction (8)),

Scheme II



and Fl^- then went on to yield the "extra" amounts of azine and FlH_2 (reactions (10) and (11)). The azine anion radical is oxidized to azine in the work-up.

In an attempt to determine the extent to which each reaction potentially produced azine, the reduction of FlN_2 was carried out and quenched with D_2O followed by acidification with 6 M hydrochloric acid. The isolated fluorene was found to contain an excess of deuterium compared to that expected for simple neutralization of FlH^- (Table V). Since it was possible that H-D exchange might have occurred during the D_2O quench and H^+ acidification of the reduction mixture, the reduction was rerun and quenched by syringe injection of excess $\text{CF}_3\text{COOD-D}_2\text{O}$. The ^1H and ^{13}C nmr analysis of the resultant fluorene showed an increase in the amount of excess deuterium (FlD_2) compared to that observed in the D_2O -quenched reaction (Table V).

To determine the efficiency of the $\text{CF}_3\text{COOD-D}_2\text{O}$ quench method, FlH_2 was allowed to react with 6 equivalents of $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in THF under similar concentration conditions used in the $\text{Na}^+\text{C}_{10}\text{H}_8^-$ reduction of FlN_2 . This reaction mixture, which should produce FlH^- , was quenched with excess $\text{CF}_3\text{COOD-}$

Table V. Calculation of Percentage Compositions of Deuterated Fluorene by ^1H and ^{13}C NMR Spectroscopy.

Sample Origin	NMR	Total Aryl ^e	Integral			^{13}C Conversion Factor ^d	FMR Calculated No. of H's at C ₉ ^e	% Composition ^f		
			C ₉	Aryl	C ₉ -D(H) ^c			FLH ₂	FLHD	FLD ₂
FLH ₂	^1H	52.5	12.0 ^g					100		
	^{13}C		4171	7098		0.588		100		
				6820		0.612		100		
FLH ₂ + PhLi; D ₂ O-CF ₃ COOD	^1H	46.0	6.5 ^g				1.24	24	76	
	^{13}C		1743	13177 ^a	1605	0.158		23	77	
				13361 ^b		0.152		21	79	
FLH ₂ + 10 R ^h D ₂ O; H ₂ O-HCl	^1H	55.0	2.8 ^g				0.45	5 ⁱ	35 ⁱ	60 ⁱ
	^{13}C		148	5022 ^a	306			5	39	56
				5407 ^b				5	37	58
FLH ₂ + 10 R ^h D ₂ O-CF ₃ COOD	^1H	50.3	2.0 ^g				0.35	5 ⁱ	25 ⁱ	70 ⁱ
	^{13}C		1105	39065 ^a	2033			5	33	62
				39505 ^b				5	34	61
FLH ₂ + 6 R ^h D ₂ O-CF ₃ COOD	^1H	60.3	6.0 ^g				0.88	3 ⁱ	72 ⁱ	20 ⁱ
	^{13}C		1268	25745 ^a	2853			8	70	22
				25540 ^b				8	73	19

^aFluorene signal at 124.5 ppm. ^bFluorene signal at 119.5 ppm. ^cIntegral of upfield peak of the C₉-D(H) triplet in proton-decoupled ^{13}C nmr spectrum. ^dRatio of [C₉-D(H)]/(^{13}C ref. aryl) corrected from 77% and 79% to 100% FLHD. ^eCalculated by [(C₉)/(total aryl)] x 3.75. ^fCalculated from the ^{13}C nmr data using [(C₉)/(ref. ^{13}C aryl)]/(conversion factor for FLH₂) = % FLH₂, and [(C₉-D(H))/(ref. ^{13}C aryl)]/(conversion factor for FLHD) = % FLHD. The % FLD₂ is calculated by difference. ^gUnit = mm. ^hR = Na⁺C₁₀H₉⁻. ⁱPercent compositions from ^1H nmr use the value of FLH₂ determined for this species by ^{13}C nmr using relative integrals of two different aryl C's and C₉-H₂ of authentic FLH₂. In the ^{13}C nmr analysis known relative integrals of these aryl C's to the triplet of authentic FLHD were used to determine the % of this species. The amount of FLD₂ was by difference.

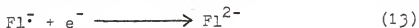
-D₂O. The isolated fluorene was found to contain considerably less F1D₂ (40-50%) than was observed in the similar reduction of F1N₂.

While the amount of F1H₂ in these samples of fluorene could be readily determined from the integral ratios of the C₉(H₂) vs. certain aryl carbons in their proton decoupled ¹³C nmr spectra, an authentic sample of F1HD was required. This compound was obtained from the reaction of F1H₂ and 10% mole excess of commercial PhLi (dissolved in 70:30 benzene-ether) in THF. The reaction mixture was quenched by syringe injection of excess CF₃COOD-D₂O. Surprisingly, the isolated fluorene was found to be a mixture of 24% F1H₂ and 76% F1HD by ¹H nmr (Table V). The ¹³C nmr spectrum of this sample agreed quite well with this composition. That a significant amount of F1H₂ was observed in this product may indicate either a measuring error, or that the commercial PhLi contains bases other than PhLi. These bases would be titrated in the total base standardization of the solution, but they may not deprotonate F1H₂ in THF.

However, this sample was still useful in determining the amount of F1HD in the fluorene products from the above reactions by correcting the integral of the upfield line of the C₉-D triplet to 100% F1HD. This is incorporated into ¹³C conversion factor for this compound in Table V.

As mentioned above, the 40-50% excess F1D₂ found in the reductions of F1N₂ must now be considered. Since a dibasic intermediate containing the fluorene skeleton is required, it is proposed that this intermediate is the fluorenylidene dianion

(Fl^{2-}), a carbene dianion. Generation of Fl^{2-} can be rationalized by the reduction of the carbene anion radical, $\text{Fl}^{\cdot-}$, according to



The possible involvement of Fl^{2-} in this scheme of the reduction of FlN_2 by excess $\text{Na}^+\text{C}_{10}\text{H}_8^{\cdot-}$ in THF deserves some further comments. The apparent absence of Fl^{2-} in reactions of FlH_2 with strong bases is of no consequence in the present instance. We would be entering the energy surface containing Fl^{2-} from a completely different direction by a one-electron reduction of $\text{Fl}^{\cdot-}$. If the ground state electronic configuration of $\text{Fl}^{\cdot-}$ is that as suggested from MINDO/3 calculations for cyclopentadienylidene anion radical, $\delta^1\pi^2$, reduction would add an electron to the singly occupied δ -orbital of $\text{Fl}^{\cdot-}$ to yield Fl^{2-} . This reductive reaction is electron transfer from $\text{Na}^+\text{C}_{10}\text{H}_8^{\cdot-}$ and thus involves no covalent bond either made or broken. It requires that $\text{Fl}^{\cdot-}$ be reduced up to a potential not much more negative than that of naphthalene in THF ($E_{p,c} = -2.46$ V, $\text{DMF-Et}_4\text{N}^+\text{Br}^-$ vs. SCE).²⁰ Otherwise the equilibrium,



would not be favorable to give the observed results.

Further, the reduction of $\text{Fl}^{\cdot-}$ must be competitive with hydrogen atom abstraction by $\text{Fl}^{\cdot-}$ from THF. This, of course, requires a reasonable lifetime for $\text{Fl}^{\cdot-}$ in this medium. This

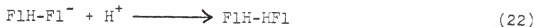
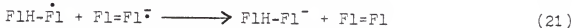
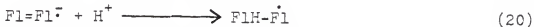
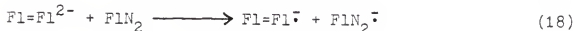
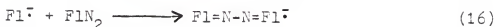
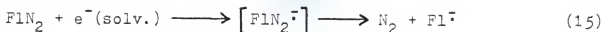
conclusion is in agreement with that from the electrochemical generation of $\text{Fl}^\cdot$ where it was proposed that the reversible red-ox couple $\text{Fl}^\cdot/\text{Fl}$ was observed in $\text{DMF}-(\text{n-Bu})_4\text{N}^+\text{ClO}_4^-$.⁸

In the electrochemical reduction of Ph_2CN_2 ,⁶ it was suggested that the sequence from $\text{Ph}_2\text{C}^\cdot$ to Ph_2CH_2 involved first hydrogen atom abstraction followed by protonation. This proposal was based on a low value of $\underline{n}$, and the absence of the resulting radical dimer, $\text{Ph}_2\text{CH}-\text{CHPh}_2$, if the reverse sequence had occurred. To test this proposed mechanistic sequence, the reduction of FlN_2 was examined in sodium in liquid ammonia. Ammonia was chosen as solvent because of its large N-H bond dissociation energy ($D_{\text{H}}^0 = 110$ or 103 kcal/mole),^{26,27} and thus should be a poor hydrogen atom donor. The pK_a of ammonia (33)²⁸ should also make it a rather poor proton donor.

The first experiment was to examine the reduction of ($\text{Fl}=\text{N}^\cdot$)₂ with an excess of solvated electrons in liquid ammonia. While no amine was produced, extensive Birch-type reduction of the fluorene ring system was evident from the nmr spectrum of the complex reaction mixture.

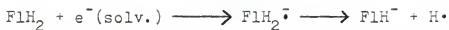
The reduction of FlN_2 was accomplished using one mole equivalent of sodium in liquid ammonia. The FlN_2 dissolved in a small amount (10 ml) of THF was rapidly syringe injected into the reducing medium (100 ml of liquid NH_3) to minimize Birch-type reduction. The products of this reduction (Table III) were ($\text{Fl}=\text{N}^\cdot$)₂ (79%), $\text{Fl}=\text{C}$ (7±1%), $\text{Fl}=\text{Fl}$ (4±1%), and FlH-HFl (5±1%). The pathways by which these products are believed to be produced are given in Scheme III.

Scheme III



Several of these results are interesting in the general understanding of the chemistry of the carbene anion radical $\text{Fl}\dot{-}$. The first is that FlH_2 is not produced under these reaction conditions. However, we cannot exclude the possibility that some hydrogen atom abstraction by $\text{Fl}\dot{-}$ did occur from the THF used to dissolve and introduce the FlN_2 to the Na/NH_3 reducing medium. Since most common solvents which are stable to Na/NH_3 behave similarly as hydrogen atom donors to phenyl radical,²¹ the only such semi-quantitative study reported, experiments involving a change from THF to another solvent were not considered at this point. Further, the 10 ml of THF was essentially the minimum quantity needed to dissolve the FlN_2 .

Although we might expect FlH_2 to be produced if $\text{FlH}\dot{-}$ was so generated and react with FlN_2 by the reactions (7) and (11) in Scheme II, it is possible that the hydrocarbon is further reduced by $e^-(\text{solv.})$ to $\text{FlH}\dot{-}$ by the reaction



This reaction sequence is known electrochemically.²⁹ Alternately, any strong bases, e.g. NaNH_2 or Fl=Fl^{2-} , present in the reduction process could abstract a proton from FlH_2 . If FlH^- was present in this reduction mixture it could also account for the formation of ketone³⁰ if oxygen was introduced during addition of the solid ammonium chloride as quench (reaction (19)). The ketone may also have been formed by O_2 oxidation of $(\text{Fl=N})_2^-$ when the solid NH_4Cl was introduced into the reduction mixture.^{23b}

The major feature of the results in liquid ammonia is the isolation of significant quantities of the olefin, 9,9'-bifluorenylidene (Fl=Fl), and its reduction product, 9,9'-bifluorenyl (FlH-HFl). While one or sometimes both of these compound have been observed previously in the reductions of FlN_2 , they have only been seen in trace quantities by glpc of reaction mixtures. Here, there appears to be no reasonable alternative but to propose dimerization of the carbene anion radical Fl^- (reaction (17)). Since the first and second reduction potentials of Fl=Fl are essentially the same as those of the $(\text{Fl=N})_2$, reaction (18) is included in Scheme III. The equal amounts of Fl=Fl and FlH-HFl could be produced by reaction (20)-(22) shown in Scheme III. Although we cannot extrapolate the present results with Fl^- to those of the proposed intermediacy of H_2C^- , the observation of dimers adds credence to Sargent's proposal that H_2C^- could dimerize in THF to produce ethylene and ethane.⁴

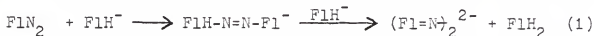
SUMMARY

Investigations of the chemical generation of diphenylcarbene anion radical ($\text{Ph}_2\text{C}^\cdot$) were carried out by reducing diphenyldiazomethane (Ph_2CN_2) with excess $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in THF under an argon atmosphere at -12°C . From the slow, dropwise addition of a THF solution of Ph_2CN_2 to a solution of $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in THF (1:5 mole ratio), product analysis showed the presence of diphenylmethane ($11\pm 2\%$; Ph_2CH_2) and benzhydrylamine ($83\pm 1\%$; Ph_2CHNH_2) along with trace amounts of tetraphenylethane ($\text{Ph}_2\text{CH-CHPh}_2$) and benzophenone azine ($(\text{Ph}_2\text{C=N})_2$) detected by glpc. Using a 10:1 ratio of Ph_2CN_2 and $\text{Na}^+\text{C}_{10}\text{H}_8^-$ gave Ph_2CH_2 (17%) and Ph_2CHNH_2 (85%). Fast, syringe injection of the THF solution of Ph_2CN_2 into the $\text{Na}^+\text{C}_{10}\text{H}_8^-$ solution (mole ratio 1:5) led to a decrease in the amount of Ph_2CH_2 ($5\pm 1\%$) while the yield of Ph_2CHNH_2 ($92\pm 1\%$) increased. The amine Ph_2CHNH_2 was shown to arise by $\text{Na}^+\text{C}_{10}\text{H}_8^-$ reduction of $(\text{Ph}_2\text{C=N})_2$. These results are compared and contrasted with those reported from the electrochemical reduction of Ph_2CN_2 in $\text{DMF}-(\text{n-Bu})_4\text{N}^+\text{ClO}_4^-$ where a chain reaction was shown to be involved.

Analogous reductions of 9-diazofluorene (FlN_2) by $\text{Na}^+\text{C}_{10}\text{H}_8^-$ (1:10 mole ratio) in THF were also examined. The slow addition method gave fluorene ($40\pm 2\%$; FlH_2) and 9-aminofluorene ($53\pm 3\%$; FlHNH_2), while the fast, syringe injection method produced the same two components in 12% and 88% yields, respectively. As in the reductions of Ph_2CN_2 , the yield of hydrocarbon, FlH_2 , decreased substantially when the mole ratio of

$\text{FlN}_2/\text{Na}^+\text{C}_{10}\text{H}_8^-$ was reduced. The amine FlHNH_2 was shown to be produced quantitatively in the reduction of azine ($\text{Fl=N}\rightarrow_2$) by $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in THF.

9-Fluorenyl anion (FlH^-) was prepared and allowed to react with FlN_2 in THF. The products were ($\text{Fl=N}\rightarrow_2$) and FlH_2 , and were believed formed by nucleophilic addition of FlH^- to the terminal nitrogen of FlN_2 in the primary reaction sequence,



The azine dianion would then be expected to reduce excess FlN_2 by electron transfer to yield $\text{Fl}\cdot$ and its further reaction products, FlH_2 and azine.

This result suggested two possible pathways for azine formation in the reduction of FlN_2 , one by reaction (1) and the second by direct coupling of $\text{Fl}\cdot$ and FlN_2 to yield ($\text{Fl=N}\rightarrow_2\cdot$). To test for the involvement of these two pathways, the slow addition method for reduction of FlN_2 with $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in THF was run with D_2O in one case and $\text{CF}_3\text{CO}_2\text{D-D}_2\text{O}$ in a second experiment added to quench the reaction. The results showed the presence of fluorene containing 60% and 70%, respectively, of excess deuterium as FlD_2 . To see if some H-D exchanges at C_9 of fluorene might have occurred in the $\text{CF}_3\text{COOD-D}_2\text{O}$ quench, the reaction of FlH_2 with $\text{Na}^+\text{C}_{10}\text{H}_8^-$ (1:6 mole ratio) in THF as in the slow addition method followed by the quench of $\text{CF}_3\text{COOD-D}_2\text{O}$ was carried out to give fluorene containing 20% of excess FlD_2 . After correction for H-D exchanges, the large excess of 40% and 50%, respectively, of excess FlD_2 indicated the for-

mation of the carbene dianion, Fl^{2-} . Generation of Fl^{2-} can be rationalized by the further reduction of Fl^- .

Reduction of FlN_2 in Na/NH_3 gave ($\text{Fl}=\text{N}^+$)₂ (79%), fluorenone (61%), 9,9'-bifluorenyl (41%; FlH-HFl) and 9,9'-bifluorenylidene (31%; $\text{Fl}=\text{Fl}$). Since ammonia should not serve as a hydrogen atom donor, the dimeric products, FlH-HFl and $\text{Fl}=\text{Fl}$, are believed to be produced by radical dimerization of $\text{Fl}^\cdot$.

EXPERIMENTAL SECTION³¹

Benzophenone Hydrazone. The procedure of Smith and Howard³² was followed to afford 37.5 g (87%), mp 97-98°C (lit.³³ 97-98°C); ir (KBr): 3350 cm⁻¹ (doublet, NH₂); nmr: $\delta_{\text{TMS}}^{\text{CCl}_4}$ 7.0-7.5 (m, aromatic H's, 10), 5.0-5.5 (s, NH₂, 2).

Diphenyldiazomethane. This compound was prepared from a mixture of 13 g (66 mmol) of benzophenone hydrazone, 15 g of anhydrous sodium sulfate, 200 ml of anhydrous ether, 10 ml of absolute ethanol saturated with potassium hydroxide, and 35 g (0.160 mol) of yellow mercuric oxide (new Fisher brand) according to the procedure of Miller⁹ except using double the volume of absolute ethanol saturated with potassium hydroxide. The mixture was shaken for 75 min. in a parr shaker. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure at about 30°C. The dark red oil obtained was dissolved in petroleum ether (bp 35-60°C) and again filtered. Removal of the solvent from the filtrate under reduced pressure at about 30°C gave an oil. Freezing this in a stopped flask with Dry Ice and then allowing the flask to warm spontaneously to room temperature gave dark red crystals in an average yield of 12.2 g (92%), mp 29-30°C (lit.³⁴ mp 29-30°C); ir (KBr): characteristic absorption at 2050 cm⁻¹ (-N⁺=N⁻); nmr: $\delta_{\text{TMS}}^{\text{CCl}_4}$ 7.3 (s, aromatic H's).

Tetraphenylethylene. This compound was obtained from Aldrich Chemical Company, mp 222-224°C (lit.³⁵ mp 220°C); ir (KBr): 1575 cm⁻¹ (C=C); nmr: $\delta_{\text{TMS}}^{\text{CCl}_4}$ 7.1 (s, aromatic H's).

Tetraphenylethane. The compound was obtained from Columbia Chemical Company and recrystallized from CHCl_3 -EtOH (1:1) with mp $210.5\text{--}211.5^\circ\text{C}$ (lit.³⁶ mp $209\text{--}211^\circ\text{C}$); ir (KBr): 3000 cm^{-1} and 2900 cm^{-1} (C-H); nmr: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.9-7.3 (m, aromatic H's, 20), 4.8 (s, CH, 2).

Benzophenone Azine. The preparation of this azine was carried out according to the procedure of Whitlock.¹⁰ The pale yellow rods, mp $162\text{--}163^\circ\text{C}$ (lit.³⁷ mp 164°C), were obtained in a 90% yield after recrystallization from ethyl acetate; ir (KBr): 1600 cm^{-1} (C=N); nmr: $\delta_{\text{TMS}}^{\text{CCl}_4}$ 7.2-7.4 (m, aromatic H's).

Benzhydrylamine. This compound was obtained from Aldrich Chemical Company, mp 12°C , in 96% purity; ir (thin film): 3300 cm^{-1} (doublet, NH_2); nmr: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.1-7.4 (m, aromatic H's, 10), 5.1 (s, CH, 1), 1.7 (s, NH_2 , 2).

Diphenylmethane. This compound was prepared from a mixture of 18.2 g of $\text{Ph}_2\text{C}=\text{O}$, 7 g of NaOH, 100 ml of triethylene glycol and 10 ml of 85% hydrazine hydrate. Distillation over sodium gave 14.0 g (83%) of pure hydrocarbon, bp $73.5^\circ\text{C}/0.6\text{ mm}$. (lit.³⁸ $154\text{--}155^\circ\text{C}/33\text{ mm}$).

Fluorenone Hydrazone. The procedure of Smith and Howard³² was followed to afford 22.4 g (52%), mp $148\text{--}150^\circ\text{C}$ (lit.³⁹ $149\text{--}150^\circ\text{C}$); ir (KBr): 3350 cm^{-1} (doublet, NH_2); nmr: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.2-7.9 (m, aromatic H's, 8), 6.2-6.6 (s, NH_2 , 2).

9-Diazofluorene. This procedure of Miller⁹ was followed to give orange-red needles, mp $94\text{--}95^\circ\text{C}$ (lit.³⁹ mp $94\text{--}95^\circ\text{C}$) in 85% yield after recrystallization from petroleum ether (bp $35\text{--}60^\circ\text{C}$).

9,9'-Bifluorenylidene. This compound was prepared from coupling of fluorenone with McMurray's reagent ($4\text{TiCl}_3\text{-LiAlH}_4$ from Alfa).^{14,15} To 100 ml of THF was slowly added 3.3 g of McMurray's reagent under an argon atmosphere. The solution was allowed to stir magnetically with formation of a dark black suspension. To this suspension 3.6 g (20 mmol) of fluorenone in 50 ml of THF was added in small portions. After the addition was complete, the mixture was heated under reflux and a positive pressure of argon for 6 hr. The cooled mixture was poured into 1.5 liters of distilled water and extracted with CCl_4 . After the solvent was removed, the residue was eluted through a column of alumina (100 g) with n-hexane to give 4.0 g of crude product. Recrystallization from $\text{CHCl}_3\text{-EtOH}$ (1:1) gave 3.0 g (91%) of 9,9'-bifluorenylidene, mp $194\text{-}195^\circ$ (lit.⁴⁰ mp 194°C); ir (KBr): 1600 cm^{-1} (C=C); nmr: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.0-7.7 (m, aromatic H's, 13.5), 8.2-8.4 (m, aromatic H's, 2.5).

9,9'-Bifluorenyl. To 2.14 g (6 mmol) of $(\text{Fl-N})_2$ in 8 ml of distilled diethylene glycol was added 0.1 g (3 mmol) of hydrazine (95%) and a solution of 1.2 g (3 pellets) of potassium hydroxide in 5 ml of diethylene glycol (prepared by brief warming in a test tube). The mixture was kept on the steam-bath for 10 min., then gently heated on a hot-plate for 3 hrs under a reflux condenser. The color changed from red-brown to dark-green. At the end of reduction period, the material in the condenser was rinsed into the flask with 5 ml of ethanol, and the mixture heated under reflux for 15 min., The mixture was allowed to cool and was acidified with 8 ml of 12 N HCl,

diluted with 50 ml of distilled water, and cooled in an ice bath. The deep-brown crude product was filtered and recrystallized three times from benzene-ethanol (1:2) to give 0.3 g (15%) of white needles of 9,9'-bifluorenyl, mp 244-245°C (lit.⁴¹ mp 246°C); ir (KBr): 3000 cm^{-1} (C-H); nmr: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.8-7.4 (m, aromatic H's, 13), 7.4-7.7 (m, aromatic H's, 4), 4.8 (s, CH, 2).

Fluorene. This compound was obtained from Eastman Organic Chemicals, mp 115-117°C. Recrystallization from ethanol afforded white needles, mp 115-117°C; ir (KBr): 2950 cm^{-1} ; nmr: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.2-7.9 (m, aromatic H's, 8.75), 3.9 (s, CH, 2).

9-Aminofluorene. 9-Aminofluorene hydrochloride (obtained from Aldrich), 99%, in ether solution was basified to pH ~13, and then extracted with ether. The ether solution was washed with distilled water, saturated sodium chloride solution, and dried (MgSO_4). Separation from solvent afforded white crude product. Recrystallization from hexane yielded 9-aminofluorene, mp 64-65°C (lit.⁴² mp 64-65°C); ir (KBr): 3350 cm^{-1} ; nmr: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.1-7.7 (m, aromatic H's, 9), 4.8 (s, CH, 1), 1.7 (s, NH_2 , 2).

Fluorenone Azine.¹³ A solution of 17.0 g of KOH in 60 ml of ethanol was added to a magnetically stirred hot mixture of 16.3 g (45 mmol) of fluorenone, 21 ml of hydrazine (95%), and 225 ml of ethanol. The whole mixture immediately turned deep-red. Formation of the azine was completely by heating under reflux for 15 min.. Upon cooling, 15.5 g (96%) of violet needles were removed by filtration. Recrystallization from xylenes

yielded 13.0 g (81%) of fluorenone azine, mp 268-269°C (lit.⁴³ mp 265°C); ir (KBr): 1600 cm^{-1} ; nmr: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.1-7.7 (m, aromatic H's, 12), 7.8-8.2 (m, aromatic H's, 4).

Preparation of Sodium Naphthalene Solution. Into a 1-l., four-necked, round-bottomed flask, 400 ml of THF (distilled from LiAlH_4 under an argon atmosphere) was distilled under argon. After addition of 12.8 g (0.10 mol) of naphthalene and 2.0 g (0.087 mol) of sodium (freshly-cut under a layer of xylene and rinsed with petroleum ether before use) the deep-green mixture was cooled to -12°C and magnetically stirred for over 24 hr under argon to insure complete reaction. Two 5-ml aliquots were removed, and each was quenched in 50 ml of water, and titrated for total base with standardized hydrochloric acid to a phenolphthalein end-point to obtain a solution approximately 62.8 mmol in $\text{Na}^+\text{C}_{10}\text{H}_8^-$.

Reaction of Diphenyldiazomethane with Sodium Naphthalene.⁴⁴

(a). Slow, Dropwise Addition. To a 62.8 mmol $\text{Na}^+\text{C}_{10}\text{H}_8^-$ solution, a solution of 3.06 g (15.7 mmol) of Ph_2CN_2 in 150 ml of THF was added dropwise over a period of one hr. After 10 min., 50 ml of water was added and the mixture turned light yellow. The solvent was removed (rotavaporator) and the residue dissolved in ether. The ether solution was separated from the aqueous layer, and the ether layer was extracted with three 100-ml portions of 10% HCl solution. The aqueous acidic solution was basified to pH~13 with 10% NaOH solution, and the alkaline solution extracted with three 100-ml portions of ether. The combined ether extracts were washed with 150 ml of dis-

tilled water followed by 150 ml of saturated NaCl solution and dried (MgSO_4). After solvent removal, 2.00 g (70%) of benzhydrylamine was obtained and identified by comparison of its nmr and ir spectra with those of an authentic sample. After correction for the preestablished recovery of this amine (83.8%), an 84% yield of benzhydrylamine was obtained. The benzamide derivative was prepared as white crystals, mp $170-171.5^\circ\text{C}$ (lit.⁴⁵ 172°C).

The original ether solution was washed with 150 ml of distilled water, 150 ml of saturated NaCl solution, and dried (MgSO_4). After removal of the solvent, the residue was separated by sublimation at $35^\circ\text{C}/0.2$ mm. The nmr spectrum of this sublimate showed only the presence of naphthalene, 1,4-dihydronaphthalene, and Ph_2CH_2 . Since the nmr absorptions of these three components are cleanly separated from one another, the amount of Ph_2CH_2 could be determined from the relative peak areas multiplied by the total weight of the sublimate. In order to get satisfactory results for Ph_2CH_2 , the sublimate was dissolved in CH_2Cl_2 and about 10 ml of this homogeneous solution removed for the nmr spectral determination. After solvent removal, the white solid was dissolved in CDCl_3 and the nmr spectrum and integrals recorded yielding 0.33 g (13%) of Ph_2CH_2 (run 1, Table I).

The experiment was repeated following the same procedures described above to give Ph_2CH_2 (10%) and Ph_2CHNH_2 (82%) (run 2, Table I). Another experiment was carried out following the same procedures as described above to give Ph_2CH_2 (17%) and

Ph_2CHNH_2 (85%) except that 3.08 g (15.8 mmol) of Ph_2CN_2 in 100 ml of THF was added dropwise to $\text{Na}^+\text{C}_{10}\text{H}_8^-$ (159 mmol) in 400 ml of THF over a period of 0.5 hr. (run 3, Table I).

(b). Fast, Syringe Injection. To $\text{Na}^+\text{C}_{10}\text{H}_8^-$ (52.2 mmol) in 200 ml of THF a solution of 2.01 g (10.4 mmol) of Ph_2CN_2 in 10 ml of THF was injection via a syringe over a period of 5 sec.. Isolation of the products as described in the slow addition method gave 0.07 g (4%) of Ph_2CH_2 and 1.74 g (91%) of Ph_2CHNH_2 (run 4, Table I).

This experiment was repeated following the same procedures to give Ph_2CH_2 (5%) and Ph_2CHNH_2 (93%) (run 5, Table I).

Reaction of Benzophenone Azine with Sodium Naphthalene.⁴⁴

Benzophenone azine (1.04 g, 2.91 mmol) in 100 ml of THF was treated in the same manner as the slow, dropwise addition of Ph_2CN_2 with $\text{Na}^+\text{C}_{10}\text{H}_8^-$ (34.9 mmol). Benzhydrylamine (0.87 g, 82%) was obtained. After correction with the recovery factor for this amine, a 98% yield for benzhydrylamine was obtained.

Reaction of 9-Diazofluorene with Sodium Naphthalene.⁴⁴

(a). Slow, Dropwise Addition. To $\text{Na}^+\text{C}_{10}\text{H}_8^-$ (156.5 mmol) in 400 ml of THF, a solution of 3.00g (15.6 mmol) of FlN_2 in 100 ml of THF was added dropwise over a period of 0.5 hr. After 10 min, 50 ml of water was added which decolorized the reaction mixture. The procedures of separation as those in the reduction of Ph_2CN_2 with $\text{Na}^+\text{C}_{10}\text{H}_8^-$ were followed to give 1.18 g (42%) of FlHNH_2 (run 1, Table II). After correction for its recovery factor (83.8%), this gave a 50% yield of FlHNH_2 . Naphthalene and 1,4-dihydronaphthalene were removed by sub-

limation and fluorene remained in the sublimation tube. Using 1,3,5-trinitrobenzene as an internal standard and integrating the nmr spectrum, 1.08 g (42%) of fluorene in the mixture was determined.

The experiment was repeated using a 151 mmol $\text{Na}^+\text{C}_{10}\text{H}_8^-$ solution in 400 ml of THF and 2.90 g (15.1 mmol) of FlN_2 in 100 ml of THF and gave FlH_2 (39%) and FlHNH_2 (55%) (run 2, Table II).

(b). Fast, Syringe Injection. To a solution of 38.8 mmol of $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in 200 ml of THF, a solution of 1.86 g (9.7 mmol) of FlN_2 in 10 ml of THF was injected via a syringe over a period of 5 sec. Isolation of the products as described above in (a) gave 1.35 g (77%) of FlHNH_2 (run 3, Table II). Naphthalene and 1,4-dihydronaphthalene were removed by sublimation and the residue was eluted through a silica gel column (100 g) with n-hexane to give 0.31 g of a mixture of compounds. Using 1,3,5-trinitrobenzene as an internal standard, the nmr spectrum of this mixture showed it to contain 0.10 g (7%) of FlH_2 . Benzene- CHCl_3 (50:50, v/v) eluted 0.10 g (6%) of $(\text{Fl}=\text{N})_2$ checked by TLC and glpc.

Another experiment was carried out by syringe injection of a solution of 2.16 g (11.3 mmol) of FlN_2 in 10 ml of THF into a solution of 112.3 mmol of $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in 200 ml of THF over a period of 5 sec. Separation of the products as described above in the slow additions of FlN_2 gave FlH_2 (12%) and FlHNH_2 (88%) (run 4, Table II).

Reaction of Fluorenone Azine with Sodium Naphthalene. ⁴⁴

A solution of 1.00 g (2.80 mmol) of $(\text{Fl}=\text{N})_2$ in 100 ml of THF was treated by the same procedure as those in the reaction of FlN_2 with 33.70 mmol of $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in 400 ml of THF, yielding 0.85 g (84%) of FlHNH_2 . After correction for its recovery factor, this gave 100% yield for FlHNH_2 .

Reaction of 9-Diazofluorene with Sodium-Ammonia. Into a 500-ml, three-necked, round-bottomed flask, 100 ml of anhydrous NH_3 (distilled from Na) was condensed under an argon atmosphere and 0.24 g (10.4 mmol) of freshly-cut Na was added. The Na- NH_3 solution was allowed to stir magnetically for 30 min. Then 1.96 g (10.2 mmol) of FlN_2 in 9.5 ml of THF was syringe injected into the reducing solution over a period of 5 sec. The whole solution turned red-blue with a precipitate of black solids. The mixture was allowed to stir for additional 3 min and quenched with solid NH_4Cl . After evaporating the NH_3 with an argon gas, 200 ml of ether was added to the flask. The mixture turned purple with a black-blue precipitate. The mixture was extracted with 800 ml of hexane and then 50 ml of CCl_4 - CHCl_3 to give deep-red solids and an orange-red solution. The deep-red solids gave 1.40 g of $(\text{Fl}=\text{N})_2$ identified by TLC and glpc. Evaporation of solvent from the orange-red solution resulted in 0.31 g of an orange solid. This orange solid was eluted through a column of silica gel (50 g) with hexane to give 0.06 g (6%) of $\text{Fl}=\text{Fl}$, with hexane- CCl_4 (1:1, v/v) to give 0.07 g (4%) of FlH-HFl , with benzene to give 0.04 g of $(\text{Fl}=\text{N})_2$, and with benzene- CH_2Cl_2 (1:1, v/v) to give 0.11 g (6%) of $\text{Fl}=0$ checked by TLC and glpc. The combined yield of $(\text{Fl}=\text{N})_2$ was

1.44 g (79%) (run 1, Table III).

The experiment was repeated and resulted in the isolation of $\text{Fl}=\text{Fl}$ (3%), FlH-HFl (5%), $(\text{Fl}=\text{N})_2$ (79%), and $\text{Fl}=\text{O}$ (7%) (run 2, Table III).

Reaction of 9-Fluorenyl Anion with 9-Diazofluorene. Into a 500-ml, three-necked, round-bottomed flask, 200 ml of THF (distilled from LiAlH_4) was distilled under an argon atmosphere. To this was added 2.08 g (12.5 mmol) of FlH_2 followed by 6 ml (10.8 mmol) of phenyllithium (1.79 M, in 70:30 benzene/ether) by syringe injection. The orange solution was allowed to stir magnetically for 15 min under an argon atmosphere at -12°C . Then, 2.10 g (10.9 mmol) of FlN_2 in 10 ml of THF was injected with syringe. The whole solution turned deep-red. After stirring for 30 min, the reaction was quenched with 20 ml of distilled water. Rotavaporation of solvent afforded deep-red solids as crude product. The mixture was eluted through a column of silica gel (150 g) with hexane to give 1.20 g (7.23 mmol) of FlH_2 , with hexane- CCl_4 (1:1, v/v) to give 0.10 g (0.3 mmol) of FlH-HFl , and with benzene to give 2.35 g (6.60 mmol) of $(\text{Fl}=\text{N})_2$ (checked by TLC and glpc). Only trace amount of $\text{Fl}=\text{Fl}$ was detected by glpc (run 2, Table IV).

The experiment was repeated with 2.12 g (11.0 mmol) of FlN_2 in 10 ml of THF to give 1.94 g (11.7 mmol) of FlH_2 and 2.31 g (6.5 mmol) of $(\text{Fl}=\text{N})_2$; FlH-HFl or $\text{Fl}=\text{Fl}$ were not detected (run 1, Table IV).

Reaction of 9-Fluorenyl Anion with $\text{CF}_3\text{COOD-D}_2\text{O}$. To 100 ml of dry, deoxygenated THF in a 500-ml, three-necked, round-

bottomed flask under an argon atmosphere at -12°C was added 2.00 g (12.0 mmol) of FlH_2 followed by syringe injection of 7.4 ml (13.3 mmol) of phenyllithium solution (1.79 M, in 70:30 benzene/ether). The orange solution was allowed to stir magnetically for 15 min under an argon atmosphere at -12°C . To this was injected a solution of $(\text{CF}_3\text{CO})_2\text{O}$ (1.96 g, 9.33 mmol) and D_2O (1.99 g, 100 mmol). The orange solution immediately turned light-yellow. After removal of the solvent, the residue was dissolved in 100 ml of ether. The ether solution was washed with two 150-ml portions of distilled water, 150 ml of saturated NaCl solution, and dried (MgSO_4). Evaporation of the solvent gave 2.10 g of white solids. Recrystallization from ethanol gave 1.90 g of white needles in a 95% yield. This compound was identified as a mixture of 22% FlH_2 and 78% FlHD by ^{13}C nmr spectrum, and 24% FlH_2 and 76% FlHD by ^1H nmr spectrum (Table V).

Reaction of Fluorene with Sodium Naphthalene.⁴⁴ To a 44.0 mmol of $\text{Na}^+\text{C}_{10}\text{H}_8^-$ in 400 ml of THF was added, dropwise, a solution of 1.20 g (7.2 mmol) of FlH_2 in 100 ml of THF over a period of 15 min at -12°C under an argon atmosphere. After 30 min, a mixture of $(\text{CF}_3\text{CO})_2\text{O}$ (10.6 g, 50.5 mmol) and D_2O (7.0 g, 350 mmol) was syringe injected to the deep-green solution over a period of 10 sec. The solution turned white after addition of the acidic quench. After 15 min, the solvent was removed by rotovaporation, and the residue was dissolved in 100 ml of ether. The ether solution was washed with two 150-ml portions of distilled water and dried (MgSO_4). Evaporation of

the solvent gave a white solid. Naphthalene and 1,4-dihydro- and -deuterionaphthalene were removed by sublimation at 30°C/-0.2 torr and light yellow solids remained in the sublimation tube. The bath temperature was raised up to 60°C and fluorene sublimed, which was recrystallized from ethanol (1.10 g) and identified as a mixture of 8% FlH₂, 72% FlHD, and 20% FlD₂ by ¹³C nmr spectrum; 8% FlH₂, 72% FlHD, and 20% FlD₂ by ¹H nmr spectrum (Table V).

Calculation of Percentage Compositions of Deuterated Fluorene by ¹H and ¹³C NMR Spectroscopy. From multiple integration of the ¹H nmr spectrum of authentic FlH₂, the total aryl-H's/-C₉-H₂ ratio was determined to be 8.75/2 (see Table V). The number of protons at C₉ of a sample of C₉-deuterated fluorene were determined from its integral ratio, (C₉/total aryl), multiplied by 8.75. Using the amount of FlH₂ found in the sample by ¹³C nmr, the %'s FlHD and FlD₂ were then calculated in the sample.

In the proton decoupled ¹³C nmr spectrum of authentic FlH₂, integrals of the C₉ and two of the aryl carbon absorptions, C_a (124.5 ppm) and C_b (119.5 ppm), were used to give C₉/C_a = 0.588 and C₉/C_b = 0.612 ratios (conversion factors, Table V). The ratios of these integrals for the deuterated fluorene were then divided by these correction factors to obtain the percent FlH₂ in this sample.

To determine the percent FlHD in the sample, the mixture of 24% FlH₂ and 76% FlHD (by ¹H nmr) was used. The ratio of the integrated upfield absorption line of the C₉-D(H) triplet to

C_a or C_b , corrected to 100% FLHD, gave the conversion factors 0.158 and 0.152, respectively (Table V). The ratio of these integrated absorptions for the deuterated fluorene samples divided by these conversion factors gave the percent of FLHD in the sample. The percent FLD_2 was then taken as the difference, $100 - \% FLH_2 - \% FLHD$.

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VITA

Kuo-Wei Lin was born in Lo-Tung, Taiwan, on March 8, 1951. He was reared in Lo-Tung, where he lived until graduation from Taipei Institute of Technology in 1971.

In the summer of 1971, he entered the navy and was discharged from military service in June, 1973. He then entered Nan Ya Plastics Corporation in Taipei. In December, 1974, he married the former Virginia Su-O of Taipei, Taiwan.

In January, 1975, he entered the Graduate School at Kansas State University. His research program in organic chemistry for the M.S. degree was directed by Dr. Richard N. McDonald.

Kuo-Wei and Virginia have one son, Christopher, born in June of 1977.

THE CHEMICAL GENERATION OF CARBENE ANION RADICALS

by

KUO-WEI LIN

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ABSTRACT

The chemical generation of diphenylcarbene anion radical (Ph_2C^-) and fluorenylidene anion radical (Fl^-) was investigated. Slow, dropwise addition of a THF solution of diphenyldiazomethane (Ph_2CN_2) to excess sodium naphthalene in THF at -12°C under an argon atmosphere gave diphenylmethane (Ph_2CH_2) ($11 \pm 2\%$) and benzhydrylamine (Ph_2CHNH_2) ($83 \pm 1\%$) along with trace amounts of tetraphenylethane and benzophenone azine. Fast, syringe injection of the Ph_2CN_2 solution into the reducing agent produced $5 \pm 1\%$ Ph_2CH_2 and $92 \pm 1\%$ Ph_2CHNH_2 .

Analogous slow, dropwise addition of 9-diazofluorene (FlN_2) in THF to excess sodium naphthalene in THF gave fluorene (FlH_2) ($40 \pm 2\%$) and 9-aminofluorene (FlHNH_2) ($53 \pm 3\%$), while fast, syringe injection gave the same components in 12% and 88% yields, respectively. The amines, Ph_2CHNH_2 and FlHNH_2 , were shown to be the further reduction products of the corresponding azines, ($\text{Ph}_2\text{C}=\text{N}-\text{N}$) $_2$ and ($\text{Fl}=\text{N}-\text{N}$) $_2$. Fast, syringe injection of FlN_2 dissolved in a small amount of THF into sodium in liquid ammonia gave $79 \pm 0\%$ ($\text{Fl}=\text{N}-\text{N}$) $_2$, $6 \pm 1\%$ fluorenone, $4 \pm 1\%$ 9,9'-bifluorenyl, and $4 \pm 1\%$ 9,9'-bifluorenylidene.

These results are rationalized in terms of the intermediacy of the two carbene anion radicals, Ph_2C^- and Fl^- . The formation of the arenes, Ph_2CH_2 and FlH_2 , is established as the sequence $\text{H}^\bullet$ followed by H^+ abstraction. Isolation of the two dimers, $\text{Fl}=\text{Fl}$ and $\text{FlH}-\text{HFl}$, from the Na/NH_3 reduction of FlN_2 demonstrates that Fl^- can dimerize if certain other reactions of the carbene anion radical are suppressed.

Addition of D_2O or $CF_3COOD-D_2O$ to the reduction mixture from slow addition of FlN_2 to sodium naphthalene in THF gave fluorene containing 40% and 50%, respectively, of excess deuterium as FlD_2 . This excess deuterium content has been corrected for some H-D exchanges of C_9 of fluorene occurring in the $CF_3COOD-D_2O$ quench of related reaction mixtures. To account for the excess deuterium, it was proposed that $Fl\cdot$ was reduced by sodium naphthalene to the carbene dianion, Fl^{2-} .

Reaction of 9-fluorenyl anion (FlH^-) with FlN_2 in THF gave FlH_2 and $(Fl=N\rightarrow)_2$. The results suggested two possible pathways for azine formation, one by reaction of FlH^- with FlN_2 and the second by direct coupling of $Fl\cdot$ and FlN_2 .